EXHIBIT A

MARKED-UP VERSION OF THE CLAIMS AMENDED

U.S. PATENT APPLICATION SERIAL NO. 09/574,836

The rewritten claims were revised as follows:

[US CLAIMS] THE CLAIMS

1. (Amended) A re-closable packaging comprising a container and a cover;[:]

wherein the [(A) a] container[, said container comprising] comprises a support layer [(1)] bearing two opposed faces, the innermost face of which is joined to a complexable layer [(2)] by optionally interposing said face on an outermost face of an optional bonding layer bearing two opposed faces;[,]

the optional bonding layer is interposed on a structure comprising: a complexable layer bearing two opposed faces, the innermost face of the optional bonding layer being interposed on the outermost face of the complexable layer,

the innermost face of the complexable layer is interposed on an outermost face of a pressure-sensitive adhesive layer [(3)] bearing two opposed faces,

the innermost face of the pressure-sensitive adhesive layer is interposed on a first face of [and] a tearable-welding layer [(4), the structure (C) comprising the layers (2), (3) and (4) being laid on the support film (1); and, facing said container, (B) a cover member or lid, said] bearing two opposed faces;

wherein the cover [member comprising] comprises a welding layer [(5)] with two opposed faces, the first face of which is

interposed on an innermost face of **[and]** a support layer **[(6),]** **bearing two opposed faces;**

wherein the second face of the **[said]** tearable-welding layer **[(4)]** and **the second face of the** **[said]** welding layer **[(5) being welded]** **are joined by welding** along a seam **[(D)]** **to form a welded seam; and**

wherein the pressure-sensitive adhesive layer optionally comprises two pressure-sensitive adhesive sub-layers.

2. (Amended) The re-closable packaging according to claim 1, in which **[said structure (C) is laid on the support layer (1) through a binding]** **the bonding** layer **[(7)]** **is present**.

3. (Amended) The re-closable packaging according to claim 2, in which said structure **[(C)]** is **[laid on]** **joined to** the support layer **[(1)]** by lamination.

4. (Amended) The re-closable packaging according to claim 3, in which the **[binding]** **bonding** layer **[(7)]** is a polyurethane adhesive.

5. (Amended) The re-closable packaging according to claim 2, in which said structure **[(C)]** is **[laid on]** **joined to** the support layer **[(1)]** by extrusion-lamination.

6. (Amended) The re-closable packaging according to claim 1, in which **[said structure (C) is laid directly on]** **the bonding layer is absent and in which the complexable layer is joined to** the support layer **[(1)]** by hot-calendering.

7. (Amended) The re-closable packaging according to claim 1, in which said container **[(A)]** is a **[rigid]** tub **[or receptacle]**.

8. (Amended) The re-closable packaging according to claim 1, in which said container **[(A)]** is a flexible receptacle.

9. (Amended) The re-closable packaging according to claim 1, in which said container **[(A)]** is thermoformed.

10. (Amended) The packaging according to claim 1, in which **the packaging is opened by** tearing **and wherein the tearing** **[at said seam]** takes place within **[said]** **the pressure-sensitive** adhesive layer **[(3)]**.

11. (Amended) The packaging according claim 1, in which the **tearable-welding layer has a first** melting point**, the pressure-sensitive adhesive layer has a second melting point, and the first melting point is greater than the second melting point** **[of the said tearable welding layer (4) is higher than that of said adhesive layer (3)]**.

12. (Amended) The re-closable packaging according to claim 1, in which said pressure-sensitive adhesive layer **[(3)]** comprises a thermoplastic elastomer-based hot melt adhesive.

13. (Amended) The re-closable packaging according to claim 1, in which said adhesive **is formed of** **[comprises]** from 5 to 25% by weight of a master batch **comprising a substance chosen from the group consisting of a** **[containing]** filler**, a** **[or]** processing agent**[s]****, and mixtures thereof**.

14. (Amended) The re-closable packaging according to claim 1, in which **the tearable-welding layer and the** **[said]** welding layer**[s (4) and (5) are in PE]** **each comprise a polyethylene**.

15. (Amended) The packaging according to claim 14, in which **[said tearable welding layers comprise]** **the polyethylene is a** metallocene **[PE]** **polyethylene**.

16. (Amended) The packaging according to claim 1, in which said complexable layer**[s (2)]** and **said** tearable-welding layer**[s (4)]** **each** have **[identical]** **the same** composition**[s]**.

17. (Amended) The packaging according to claim 1, in which **the pressure-sensitive adhesive layer optionally comprises two pressure-sensitive adhesive** **[said structure (C) comprising said layers (2), (3), and (4) is symmetrical in composition, said adhesive layer (3) comprising two]** sub-layers **[(3a, 3b)]**, **each sub-layer having the same composition**.

18. (Amended) The packaging according to claim 17, in which said structure **[(C)]** is obtained by collapsing **[the]** **a** co-extrusion bubble.

19. (Amended) The packaging according to claim 18, in which **[said collapsing of]** the co-extrusion **bubble is collapsed in an** **[done under]** oxidizing **[conditions]** **medium**.

20. (Amended) A re-closable packaging comprising**[:]** **a container and a cover;**

wherein the [(A) a] container**[, said container comprising]** **comprises** a support layer **[(1)]** **bearing two opposed faces**, **the innermost face of which is joined to an outermost face of a bonding** [binding] layer **[(7)]** **bearing two opposed faces by laminating;**[,]

the bonding layer is interposed on a structure comprising: a complexable layer **[(2)]** **bearing two opposed**

faces, the innermost face of the bonding layer being interposed on the outermost face of the complexable layer,

the innermost face of the complexable layer is interposed on an outermost face of a pressure-sensitive adhesive layer [(3)] bearing two opposed faces,

the innermost face of the pressure-sensitive adhesive layer is interposed on a first face of [and] a tearable-welding layer [(4), the structure (C) comprising the layers (2), (7), (3) and (4) being laminated on the support film (1); and, facing said container, (B) a cover member or lid, said] bearing two opposed faces;

wherein the cover [member comprising] comprises a welding layer [(5)] with two opposed faces, the first face of which is interposed on an innermost face of [and] a support layer [(6),] bearing two opposed faces;

wherein the second face of the [said] tearable-welding layer [(4)] and the second face of the [said] welding layer [(5) being welded] are joined by welding along a seam [(D)] to form a welded seam; and

wherein the pressure-sensitive adhesive layer optionally comprises two pressure-sensitive adhesive sub-layers.

21. (Amended) The re-closable packaging according to claim 20, in which the [binding] bonding layer [(7)] is a polyurethane adhesive.

22. (Amended) The re-closable packaging according to claim 20, in which said container [(A)] is thermoformed.

23. (Amended) The packaging according to claim 20, in which the packaging is opened by tearing and wherein the tearing [at said seam] takes place within [said] the pressure-sensitive adhesive layer [(3)].

24. (Amended) The re-closable packaging according to claim 20, in which said pressure-sensitive adhesive layer **[(3)]** comprises a thermoplastic elastomer-based hot melt adhesive.

25. (Amended) The re-closable packaging according to claim 20, in which <u>**the tearable-welding layer and the**</u> **[said]** welding layer**[s (4) and (5) are in PE]** <u>**each comprise a polyethylene**</u>.

26. (Amended) The packaging according to claim 20, in which said structure **[(C)]** is obtained by collapsing **[the]** <u>**a**</u> co-extrusion bubble.

EXHIBIT B

CLEAN FORM OF ALL THE CLAIMS AS AMENDED

U.S. PATENT APPLICATION SERIAL NO. 09/574,836

THE CLAIMS

1. (Amended) A re-closable packaging comprising a container and a cover;

wherein the container comprises a support layer bearing two opposed faces, the innermost face of which is joined to a complexable layer by optionally interposing said face on an outermost face of an optional bonding layer bearing two opposed faces;

the optional bonding layer is interposed on a structure comprising: a complexable layer bearing two opposed faces, the innermost face of the optional bonding layer being interposed on the outermost face of the complexable layer,

the innermost face of the complexable layer is interposed on an outermost face of a pressure-sensitive adhesive layer bearing two opposed faces,

the innermost face of the pressure-sensitive adhesive layer is interposed on a first face of a tearable-welding layer bearing two opposed faces;

wherein the cover comprises a welding layer with two opposed faces, the first face of which is interposed on an innermost face of a support layer bearing two opposed faces;

wherein the second face of the tearable-welding layer and the second face of the welding layer are joined by welding along a seam to form a welded seam; and

wherein the pressure-sensitive adhesive layer optionally comprises two pressure-sensitive adhesive sub-layers.

2. (Amended) The re-closable packaging according to claim 1, in which the bonding layer is present.

3. (Amended) The re-closable packaging according to claim 2, in which said structure is joined to the support layer by lamination.

4. (Amended) The re-closable packaging according to claim 3, in which the bonding layer is a polyurethane adhesive.

5. (Amended) The re-closable packaging according to claim 2, in which said structure is joined to the support layer by extrusion-lamination.

6. (Amended) The re-closable packaging according to claim 1, in which the bonding layer is absent and in which the complexable layer is joined to the support layer by hot-calendering.

7. (Amended) The re-closable packaging according to claim 1, in which said container is a tub.

8. (Amended) The re-closable packaging according to claim 1, in which said container is a flexible receptacle.

9. (Amended) The re-closable packaging according to claim 1, in which said container is thermoformed.

10. (Amended) The packaging according to claim 1, in which the packaging is opened by tearing and wherein the tearing takes place within the pressure-sensitive adhesive layer.

11. (Amended) The packaging according claim 1, in which the tearable-welding layer has a first melting point, the pressure-sensitive adhesive layer has a second melting point, and the first melting point is greater than the second melting point.

12. (Amended) The re-closable packaging according to claim 1, in which said pressure-sensitive adhesive layer comprises a thermoplastic elastomer-based hot melt adhesive.

13. (Amended) The re-closable packaging according to claim 1, in which said adhesive is formed of from 5 to 25% by weight of a master batch comprising a substance chosen from the group consisting of a filler, a processing agent, and mixtures thereof.

14. (Amended) The re-closable packaging according to claim 1, in which the tearable-welding layer and the welding layer each comprise a polyethylene.

15. (Amended) The packaging according to claim 14, in which the polyethylene is a metallocene polyethylene.

16. (Amended) The packaging according to claim 1, in which said complexable layer and said tearable-welding layer each have the same composition.

17. (Amended) The packaging according to claim 1, in which the pressure-sensitive adhesive layer optionally comprises two pressure-sensitive adhesive sub-layers, each sub-layer having the same composition.

18. (Amended) The packaging according to claim 17, in which said structure is obtained by collapsing a coextrusion bubble.

19. (Amended) The packaging according to claim 18, in which the co-extrusion bubble is collapsed in an oxidizing medium.

20. (Amended) A re-closable packaging comprising a container and a cover;

wherein the container comprises a support layer bearing two opposed faces, the innermost face of which is joined to an outermost face of a bonding layer bearing two opposed faces by laminating;

the bonding layer is interposed on a structure comprising: a complexable layer bearing two opposed faces, the innermost face of the bonding layer being interposed on the outermost face of the complexable layer,

the innermost face of the complexable layer is interposed on an outermost face of a pressure-sensitive adhesive layer bearing two opposed faces,

the innermost face of the pressure-sensitive adhesive layer is interposed on a first face of a tearable-welding layer bearing two opposed faces;

wherein the cover comprises a welding layer with two opposed faces, the first face of which is interposed on an innermost face of a support layer bearing two opposed faces;

wherein the second face of the tearable-welding layer and the second face of the welding layer are joined by welding along a seam to form a welded seam; and

wherein the pressure-sensitive adhesive layer optionally comprises two pressure-sensitive adhesive sub-layers.

21. (Amended) The re-closable packaging according to claim 20, in which the bonding layer is a polyurethane adhesive.

22. (Amended) The re-closable packaging according to claim 20, in which said container is thermoformed.

23. (Amended) The packaging according to claim 20, in which the packaging is opened by tearing and wherein the tearing takes place within the pressure-sensitive adhesive layer.

24. (Amended) The re-closable packaging according to claim 20, in which said pressure-sensitive adhesive layer comprises a thermoplastic elastomer-based hot melt adhesive.

25. (Amended) The re-closable packaging according to claim 20, in which the tearable-welding layer and the welding layer each comprise a polyethylene.

26. (Amended) The packaging according to claim 20, in which said structure is obtained by collapsing a coextrusion bubble.

27.-33. Canceled without prejudice.

34. (New) A method for producing a re-closable packaging, the packaging comprising a container and a cover:

wherein the container comprises a support layer bearing two opposed faces, the innermost face of which is joined to a complexable layer by optionally interposing said face on an outermost face of an optional bonding layer bearing two opposed faces;

the optional bonding layer is interposed on a structure comprising: a complexable layer bearing two opposed faces, the innermost face of the optional bonding layer being interposed on the outermost face of the complexable layer,

the innermost face of the complexable layer is interposed on an outermost face of a pressure-sensitive adhesive layer bearing two opposed faces,

the innermost face of the pressure-sensitive adhesive layer is interposed on a first face of a tearable-welding layer bearing two opposed faces;

wherein the cover comprises a welding layer with two opposed faces, the first face of which is interposed on an innermost face of a support layer bearing two opposed faces;

wherein the method comprises:

(i) making the structure, comprising the support layer, the complexable layer and the pressure-sensitive adhesive layer;

(ii) making the support layer of the container;

(iii) joining the structure to the support layer; and

(iv) sealing the tearable-welding layer to the welding layer by welding along a seam.

35. (New) The method for producing a packaging according to claim 34, further comprising joining the structure is to the support layer by laminating.

36. (New) The method for producing a packaging according to claim 34, further comprising joining the structure to the support layer by extrusion-laminating.

37. (New) The method for producing a packaging according to claim 34, further comprising joining the structure to the support layer by hot-calendering.

38. (New) The method for producing a packaging according to claim 34, further comprising preparing the structure by collapsing a co-extrusion bubble.

39. (New) The method according to claim 34, further comprising sealing done by die pressing between two sealing jaws, only one jaw at the cover member side being heated.

EXHIBIT C

MARKED-UP VERSION OF THE SPECIFICATION PARAGRAPHS AMENDED

U.S. PATENT APPLICATION SERIAL NO. 09/574,836

The paragraph at page 4, line 1 is revised as follows:
adhesive layer (3) and a tearable welding layer (4); and, facing **the tearable welding layer of (A)** **[said]** **is the** container

The paragraph at page 4, line 3 is revised as follows:

(A′) **[a container, said]**, **that** container comprising a support layer (1'), a complexable layer (2′), a pressure-sensitive adhesive layer (3′) and a tearable welding layer (4′) **where the tearable welding layer (4′) of (A′) faces the tearable welding layer (4) of (A)**;

The paragraph at page 4, line 7 is revised as follows:

said tearable welding layers **[(4) and (4′)]** being welded along a seam (D).

The paragraph at page 4, line 9 is revised as follows:

According to one embodiment of the second type of re-closable packaging, said containers **[(A) and (A′)]** form the same structure closed about itself.

The paragraph at page 4, line 12 is revised as follows:

According to one embodiment of the second type of re-closable packaging, said containers **[(A) and (A′)]** are flexible films.

The paragraph at page 4, line 18 is revised as follows:

In a further embodiment of the re-closable packaging, the melting point of the said tearable welding layer **[(4, 4′)]** is

higher than that of said adhesive layer **[(3, 3')]**. The term "melting point" as regards the adhesive is intended to mean its softening point.

The paragraph at page 4, line 23 is revised as follows:

According to a further embodiment of the packaging, said pressure-sensitive adhesive layer **[(3, 3')]** comprises a thermoplastic elastomer-based hot melt adhesive.

The paragraph at page 4, line 29 is revised as follows:

According to a further embodiment of the packaging, said welding layers **[(4, 4') and (5, 5') are in PE]** <u>**comprise polyethylene**</u>.

The paragraph at page 5, line 1 is revised as follows:

The complexable layers **[(2, 2')]** and tearable welding layers **[(4, 4')]** preferably have identical compositions.

The paragraph at page 5, line 3 is revised as follows:

In a further embodiment of the re-closable packaging, said structure **[(C, C')]** comprising said layers **[(2, 2'), (3, 3'), and (4, 4')]** <u>**(2), (3) and (4)**</u> is symmetrical in composition, said <u>**pressure-sensitive**</u> adhesive layer (3, 3') comprising two <u>**pressure-sensitive adhesive**</u> sub-layers **[(3a, 3b), (3'a, 3'b)]**.

The paragraph at page 5, line 8 is revised as follows:

According to one embodiment of the re-closable packaging, said structure **[(C, C')]** is obtained by collapsing the co-extrusion bubble.

The paragraph at page 5, line 14 is revised as follows:

The invention also provides a method for producing a packaging according to the invention, comprising sealing said welding layers (4) and (5) **[or (4) and. (4')]**.

The paragraph at page 5, line 17 is revised as follows:

In one embodiment of the method, said structure **[(C, C')]**, comprising said support layer (1), said complexable layer (2) and said pressure-sensitive adhesive layer (3) is prepared first after which said container **[(A, A')]** is prepared.

The paragraph at page 5, line 22 is revised as follows:

In one embodiment of the method, said structure **[(C, C')]** is laminated onto said container **[(A, A')]**.

The paragraph at page 5, line 24 is revised as follows:

In another embodiment of the method, said structure **[(C, C')]** is prepared by collapsing the co-extrusion bubble.

The paragraph at page 6, line 16 is revised as follows:

FIG. 1 illustrates the packaging in one embodiment of the invention, after welding. This packaging comprises a container (A) and a lid (B). Container (A) comprises a support layer (1), **[a]** <u>**an optional**</u> complexable layer (2), a pressure-sensitive adhesive layer (3) and a tearable welding layer (4). The container can also comprise, between the support layer (1) and the complexable layer (2) a bonding layer (7), if necessary. One sub-portion of this container (A) is the structure (C), which comprises the layers (2), (3) and (4). Lid **[(3)]** <u>**(B)**</u> comprises a support layer (6) and a welding layer (5) <u>**bonded together by optional bonding layer (8)**</u>. The tearable welding layer (4) and welding layer (5) face each other. Lid (B) is welded to container (A) for

example by die pressing, using sealing jaws of which preferably only one is a heating jaw, the latter being disposed at the lid side. In **[the welding region, in]** other words**[seam (D)]**, deformation of container and lid occurs **in the welding region, seam (D)**. This deformation is characterised by a reduction and/or modification in thickness, due to

The paragraph at page 7, line 1 is revised as follows:
softening and/or melting of certain layers which leads to creep of their components over the edges of the welding seam. The welding region (seam (D)) delimits the weakened region. Support layer (6) of the lid (B) is in general little affected by welding, as the components of the support layer have a melting point which is generally distinctly higher than that of the components of the welding layer (5). The same generally applies to bonding layer **[(A)]** **(8)** of the lid. The above remarks similarly apply to support layer (1) and bonding layer (7) of container (A), which, additionally, are further from the source of heat in the preferred case where only one heated sealing jaw is used at the lid side.

The paragraph at page 7, line 14 is revised as follows:

Welding conditions (time, temperature, pressure) are set conventionally so that deformation is located at the tearable welding layer (4) and welding layer (5). As adhesive layer (3) is generally malleable **[in view of]** **by** its nature, and generally represents a relatively insignificant thickness of structure (C), there would generally not be melting or creep (lateral flow) throughout the totality of the thickness. As the adhesive layer substantially supports all of the deformation, complexable layer (2) will consequently, generally, not be deformed and consequently not weakened. The weakening, at the welding seam, is consequently principally

generated in the tearable welding layer (4), and possibly, partially in adhesive layer (3). Welding layer (5) is not fragile and its tear strength is greater than that of layer (4), as well as the cohesive strength of adhesive layer (3). When the packaging is opened, stresses propagate and bring about rupture at the most fragile layers, in other words the tearable welding layer (4) and a part of the thickness of the adhesive layer.

The paragraph at page 8, line 1 is revised as follows:

FIG. 2 shows the packaging according to the invention after opening. Tearing occurs at both sides of the welding seam (D) (the regions where the jaws operate), the effect of which is to uncover a strip composed of the torn tearable welding layer (9) and a part (10) of **pressure sensitive** adhesive layer (3), which remains welded to the welding layer of lid (B). **After opening, a** [A] part of **pressure sensitive** adhesive layer (3) providing for re-sealing, is located on each one of the inner faces of container (A) and lid (B) of the packaging. It is now sufficient to reposition the two regions corresponding to the tear face-to-face and to exercise pressure in order to re-close the packaging. The re-sealing force (re-bonding of the adhesive to itself) is proportional to the pressure exercised for re-closing. In general, tearing in the adhesive layer leads to the latter appearing slightly cloudy due to surface irregularity of the rupture giving an iridescent effect. Re-sealing is now at a maximum when the pressure exerted renders the tear region again transparent. In effect, in this case, the continuity of the adhesive layer has been reconstituted, and this adhesive layer no longer shows any surface iridescence. Reopening and re-closing are identical to the operations described above.

The paragraph at page 9, line 19 is revised as follows:

In the case where flexible pouches or bags are produced, the multilayer film forming container (A) is welded to itself. **In this case, the** [The] packaging **can** now **be thought of as comprising** [comprises] two **joined** containers**, one** (A) **on one side of the weld** and **the other** (A') **on the opposite side of the weld, each** having the same configuration. The mechanism of operation is the same as above. Also in this case, a system of sealing jaws which only apply heat on the one side will preferably be used. The portion located at the heated sealing jaw side undergoes die pressing whereas the one at the unheated side does not undergo this. In this way, upon opening, only the tearable welding layer that was situated at the heated side tears, and opening is consequently better defined. Thus, the situation is now identical to the one described previously. Container (A') could also comprise a bonding layer (7'), just like container (A). Generally, where

The paragraph at page 10, line 1 is revised as follows:
flexible bags are produced, elements (A) and (A') are formed [of] **from** the same structure.

The paragraph at page 10, line 3 is revised as follows:

It is clear that the complexable layer **(2)** is not essential and can be omitted, for example where the sheet from which container (A) is produced has been made by extrusion. In this case, adhesive (3) will be provided directly on the support (1). In the case of co-extrusion, one can for example produce a tearable multilayer of the PET or PS type, or a PP/hot melt type adhesive/PE multilayer on a suitable line (such as a (flat) cast co-extrusion line able to produce heat-shapeable semi-rigid sheets of the order of 500 μm). In the case of calendering, the complexable layer is generally present and one can first co-extrude a triple layer film

comprising complexable PE/hot melt adhesive/tearable PE, and apply it, a bit further on, to a support film, for example a PVC film (in such a case the complexable layer is not corona treated). The support film leaving the calendar is still hot (just like, generally, the extruded triple layer film) when the triple layer film is applied. This ensures maximum avoidance of deformation of the support sheets, such as PVC sheets. Adhesion of the double layer film is improved when application thereof is done using a calendar. The final multilayer product can then be subject to hot forming or another treatment, if necessary. As against this, this complexable double layer will be generally present when the sheet from which container (A) is made is produced by a lamination process.

The paragraph at page 11, line 10 is revised as follows:

Complexable layer (2) (or layer for lamination) is located on the inner face and is designed to be bonded to the support layer (1), optionally through a **[binding]** **<u>bonding</u>** layer (7). This complexable layer will advantageously be Corona discharge treated (especially in case of lamination), preferably such that its surface tension is greater than 38 dynes. This layer is conventionally **[in]** **<u>a</u>** polyolefin. Corona treatment facilitates keying of complexable layer (2) to support layer (1), preferably via a bonding layer (7); notably, this layer is an adhesive. Complexable layer (2) thus makes it possible:

The paragraph at page 12, line 4 is revised as follows:

This complexable layer is **[in]** a polyolefin. This term**<u>,</u>** **<u>i.e., polyolefin,</u>** should be taken in its normally acceptable sense in the art. By way of examples we can cite homopolymers and copolymers of olefins, with other olefins or other types of monomer (such as vinyl acetate, alkyl (meth)acrylate**<u>)</u>**.

Specific examples are: PE (such as: HDPE, MDPE, LMDPE, LDPE, LLDPE, VLDPE, metallocene PE), PP, copolymers of PE with an alpha-olefin, EVA copolymers, etc.

The paragraph at page 13, line 1 is revised as follows:
layer (4) is generally greater than that of **[adhesive]** **<u>welding</u>** layer (5).

The paragraph at page 13, line 6 is revised as follows:

This layer is generally **[in]** a polyolefin; the polyolefin can notably be the same as the one employed for the complexable layer.

The paragraph at page 13, line 9 is revised as follows:

This tearable welding layer, being on the outside, will advantageously have good machinability, obtained, for example, by adding slip and anti-blocking agents facilitating sliding over the elements of the packaging machine. Such sliding will in particular be appreciated when using vertical machines. (Ks $\leq$ 0.25**[)]**, where Ks is the static coefficient of sliding). This welding layer will advantageously have hot adhesive properties (or hot resistance properties) even while the weld or seal is still hot: the seal will not re-separate when the product to be packaged falls into the bag (in the case of a vertical machine) and/or when a gas is injected from the thermoforming machine (in other words said welding layer advantageously has "hot tack" properties). For this latter property, metallocene PE will advantageously be added to the said welding layer. The formulation of this tearable welding layer will also preferably be adjusted to prevent a tacky feel, in order to avoid all undesirable sticking or any contamination by the packaged product. The fillers that can be added in order to encourage tearing are inorganic fillers, such as talc and calcium carbonate, present in amounts

comprised for example between 5 and 30%, preferably between 5 and 15%.

The paragraph at page 16, line 17 is revised as follows:

≤ 30% of other constituents: **[plastifying]** **<u>plasticizing</u>** oil, anti-oxidation agents, additives etc.

The paragraph at page 17, line 13 is revised as follows:

It is also desirable that a multilayer film comprising a layer and an adhesive as above, may be transformed. One will consequently preferably choose adhesives of sufficiently high viscosity to avoid, or limit to the maximum **<u>extent</u>**, creep (which would otherwise lead to deformations such as variations in thickness, formation of "waves", etc) as well as flow of adhesive between the layers during thermoforming and its flowing onto the welding equipment.

The paragraph at page 18, line 22 is revised as follows:

Several processes can be used to prepare structure (C). These processes comprise cast extrusion (flat exclusion), blown film extrusion (blown bubble extrusion), etc. One valuable process is the blown film extrusion process in which, preferably, structure (C) is obtained by collapsing the co-extrusion "bubble". This embodiment is shown in FIG. 3. This **<u>embodiment</u>** produces a symmetrical structure, **<u>wherein</u>** the complexable **<u>layer (2)</u>** and tearable welding **<u>layer (4)</u>** **[layers having]** **<u>have</u>** the same composition. **<u>If</u>** **[Similarly,]** adhesive layer (3) **<u>comprises</u>** **[becomes]** two sub-layers (3a) and (3b) **[(]**respectively, **<u>then, in such embodiment,</u>** layer (3′) **<u>would also comprise</u>** **[comprises]** two **<u>corresponding</u>** sub-layers**<u>: (3a)′ and (3b)′</u>** **[(3′a, 3′b))]**. **<u>In any event, there</u>** **[There]** is now a region of weakness between **<u>the</u>** **[these]**

The paragraph at page 19, line 1 is revised as follows:

two **[sub-]**layers **<u>where 3 abuts 3'</u>**; in effect, in the re-adhesion region, the adhesive resin adheres to itself whereas in the case of one layer, the latter has been obtained by melting, leading to the formation of a homogeneous mass which is stronger thanks to its elastomeric nature. Using collapsing of the bubble, the need to modify the composition of the pressure-sensitive adhesive to be absolutely sure of achieving ready tearing within the body of the adhesive layer becomes superfluous.

The paragraph at page 19, line 10 is revised as follows:

When extruding the tube, air is generally employed for blowing (expanding) the bubble and for cooling it. The air produces a slight surface oxidation of the (hot melt) adhesive layer prior to re-bonding. The force needed to achieve tearing in the adhesive layer is smaller in the region where the layers have been rebonded, due to the slight surface oxidation thereof, compared to that within the actual layers Such oxidation can further be favored by injecting an oxidizing agent at the bubble. Ozone taken from the Corona discharge treatment equipment can **[the]** **<u>be</u>** employed as **[be]** **<u>the</u>** oxidizing agent.

The paragraph at page 21, line 26 is revised as follows:

For the support film, one can employ polyolefins (**[PP-]**cast **<u>PP</u>**, oriented PP, PE), polyamides (**[PA-]**cast **<u>PA</u>**, copolyamide, **[mono-or]** **<u>mono- or</u>** bi-oriented PA), styrenic plastics (crystalline PS, impact PS, oriented PS), PVC, impregnated or non-impregnated papers, polyesters (**[PET-]**cast **<u>PET</u>**, oriented PET, crystallizable PET, PET G), aluminum, impregnated films (impregnated with PVDC, PVA, **[...]** **<u>and the like</u>**),

The paragraph at page 22, line 1 is revised as follows:
vacuum packaging metallized films (aluminum-based, in alumina, SiO_x, **[...]** **<u>and the like</u>**).

The paragraph at page 22, line 3 is revised as follows:

Structure (C) is **[preferablt]** **<u>preferably</u>** laid on the support. According to this embodiment, the structure (C) is first prepared, notably by co-extruding, then this structure is applied onto the support by various techniques. It is possible to lay on this structure (C) by lamination, extrusion-lamination, hot-calendering or extrusion-coating. Depending on the technique used, the complexable layer receives **[or nor a supplementary]** **<u>an optional bonding</u>** **[binding]** layer.

The paragraph at page 22, line 11 is revised as follows:

In the first two techniques **[abobe]** **<u>above</u>**, a bonding layer (7) is present between the structure of the invention and the support and provides adhesion.

The paragraph at page 22, line 14 is revised as follows:

In case of lamination, structure (C) is prepared, notably by coextrusion, then laid on the support, notably under cold conditions (*i.e.* a temperature below the melt temperature of the various films). The **[binding]** **<u>bonding</u>** layer can be an adhesive or glue, notably a polyurethane adhesive or glue, especially of the polyether or polyester type, in a solvent or not. A corona treatment of the complexable layer is preferred.

The paragraph at page 22, line 22 is revised as follows:

In case of extrusion-lamination, structure (C) is prepared, notably by coextrusion, then laid on the support, (notably under cold conditions), a **[binding]** **<u>bonding</u>** layer

being placed between the structure (C) and the support, preferably by extrusion. This bonding layer can be a coextrusion binder of the type disclosed above. This binder will have preferably a melt temperature below the one of the support layer. Extrusion-lamination is similar to lamination, except that a binder is used in lieu of a glue. A corona treatment of the complexable layer is possible but optional.

The paragraph at page 23, line 1 is revised as follows:

In case of hot-calendering, structure (C) is prepared, notably by coextrusion, then directly applied onto the support (1), **[though]** **through** calenders, which heat the previously prepared films. The layers being hot, they will adhere to each other. **In this case, although it is possible, it** **[There]** is not **[necessarily, in this case,]** **necessary to use** a supplementary **[binding]** **bonding** layer (7) **[(albeit this is possible)]**, the complexable layer (2) being sufficient to ensure binding. This complexable layer can be e.g. a high content EVA layer. A corona treatment of the complexable layer is not necessary, it is **[even]** not **even desirable** **[desired]**.

The paragraph at page 23, line 11 is revised as follows:

In case of extrusion-coating, the structure (C) coextruded still hot (optionally with a supplementary **[binding]** **bonding** layer) is applied, while still hot, directly onto the support (e.g. a PET film).

The paragraph at page 23, line 15 is revised as follows:

It is preferred that the assembly formed of all **[layer]** **layers** of the structure, the **[binding]** **bonding** layer and the support are not coextruded together, in opposition to the prior art.

The paragraph at page 23, line 21 is revised as follows:

The lid comprises the support film (6) of the type described above, and the welding layer (5) of the type also described above. The tearable welding layer (4) and welding layer (5) will have the same composition, or differing compositions (while still however being compatible). These layers (6) and (5) can be bonded together, if necessary, by means of a **[binder]** **<u>bonding</u>** layer (8). This binder can be of the same type as that described above.

The paragraph at page 24, line 25 is revised as follows:

Master batch additives: slip agent, anti-blocking agent and **[anti-oxydant]** **<u>antioxidant</u>** (5%)

EXHIBIT D

NEW ABSTRACT

U.S. PATENT APPLICATION SERIAL NO. 09/574,836

ABSTRACT

The invention relates to a re-closable packaging comprising a container and a cover. The container comprises a support layer bearing two opposed faces, the innermost face of which is joined to a complexable layer by optionally interposing said face on an outermost face of an optional bonding layer bearing two opposed faces. The optional bonding layer is interposed on a structure comprising: (1) a complexable layer bearing two opposed faces, the innermost face of the optional bonding layer being interposed on the outermost face of the complexable layer, the innermost face of the complexable layer is interposed on an outermost face of (2) a pressure-sensitive adhesive layer bearing two opposed faces, the innermost face of the pressure-sensitive adhesive layer is interposed on a first face of (3) a tearable-welding layer bearing two opposed faces. The cover comprises a welding layer with two opposed faces, the first face of which is interposed on an innermost face of a support layer bearing two opposed faces. The second face of the tearable-welding layer and the second face of the welding layer are joined by welding along a seam to form a welded seam. Optionally, the pressure-sensitive adhesive layer comprises two pressure-sensitive adhesive sub-layers.

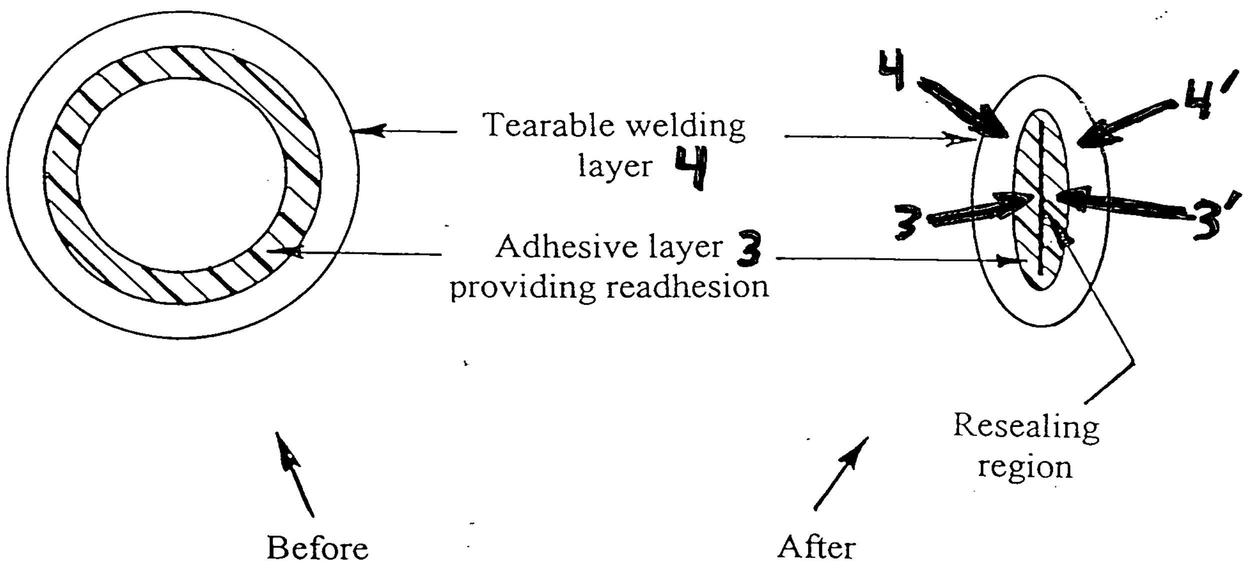
Tearable welding
layer 4
Adhesive layer 3
providing readhesion
4
4'
3
3'
Resealing
region
Before
After

FIG.3

Appendix I Symbols

Symbols

Å	Angstrom unit (10^{-8} cm)
A	Area
A	Arrhenius constant
A	Lewis acid (cationic polymerization)
A·	Antioxidant free radical
AA	Reactant (step reactions)
ABS	Copolymer from acrylonitrile, butadiene, and styrene
Ac	Acetyl group
AH	Antioxidant
ANSI	American National Standards Institute (formerly American Standards Association)
Ar	Aryl group
AR	Polyacrylate
ASTM	American Society for Testing Materials
ATR	Attenuated total reflectance spectroscopy
AU	Polyurethane
AXF	Poly(diphenylethane)
a_t	Relaxation time
$\mathcal{A}$	Arbitrary constant
$\mathcal{A}$	Exponent in Mark-Houwink equation
$\mathcal{A}_t$	Shift factor
B	Boron atom

Symbols

M	Monomer (chain reaction)
M	Quantum number
M·	Free-radical chain
Me	Methyl radical
MF	Melamine-formaldehyde resin
MR	Molar refraction
MVT	Moisture vapor transmission
m	Consistency factor (power law)
m	Meta isomer
m	Meter
m	Mole fraction of reactants (copolymers)
m	Number of mers in polymer chain
ml	Milliliter
mp	Melting point
N	Nitrogen atom
N	Number of units or items
NBR	Poly(butadiene-co-acrylonitrile)
NMR (nmr)	Nuclear magnetic resonance spectroscopy
N_n	Number average molecular weight
NR	Natural rubber
n	Index of flow (power law)
n	Index of refraction
n	Mole (step reactions) fraction
n	Normal (continuous chain, linear)
n	Number of mers in polymer chain
n	Numbers of theoretical plates
n	Ratio of mers in copolymer
nm	Nanometers (millimicrons)
O	Oxygen atom
o	Ortho isomer
oz	Ounce
P	Phosphorus atom
P	Polymer chain
P·	Polymer radical
P	Pressure
P	Resonance-stability factor (Alfrey-Price equation)
PA	Polyamide (nylon)
PC	Polycarbonate
PE	Polyethylene
PETP	Poly(ethylene terephthalate)

Introduction to Polymer Chemistry

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Introduction to Polymer Chemistry

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Some are similar to waterproofed Portland cement while others are Portland cement mixed with hydrated lime, crushed limestone, diatomaceous earth, or granulated slag.

mass. The quantity of matter contained in a particle or body regardless of its location in the universe. Mass is constant, whereas weight is affected by the distance of a body from the center of the earth (or of any other planet or satellite, e.g., the moon). At extremely high temperatures (for example, the sun's interior), mass is converted into energy. According to the Einstein equation $E = mc^2$, all forms of energy, such as radiant energy and energy of motion, possess a mass equivalent, even though they have no independent rest mass (photons); thus there is no absolute distinction between mass and energy.
See energy; matter.

mass action law. The rate of a chemical reaction for a uniform system of constant temperature is proportional to the concentrations of the substances reacting.
See chemical laws (1).

mass conservation law. See chemical laws (4).

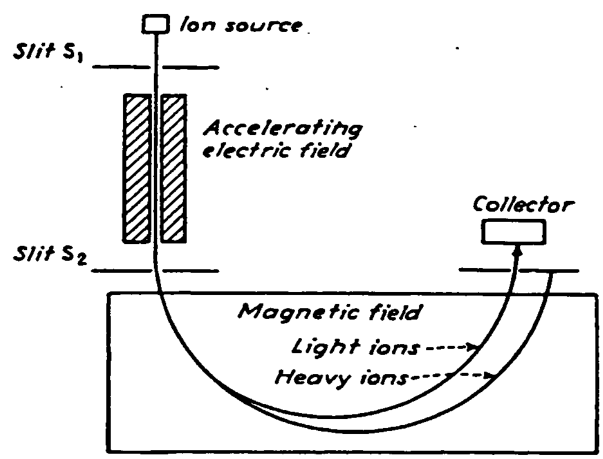
mass defect. The difference between the total mass of the constituents of an atomic nucleus (protons and neutrons) taken independently, and the actual mass of the nucleus as a whole. The latter is always slightly less than the sum of the masses of the constituents, the difference being the mass equivalent of the energy of formation (binding energy) of the nucleus. This accounts for the high energy release obtained from nuclear fission.
See fission, nuclear; mass number.

massecuite. Term used in the sugar industry for the mixture of sugar and molasses prior to removal of the molasses.

massicot. PbO. (1) (Lead ocher) Natural lead monoxide, PbO. Contains 92.8% lead; found in U.S. (Colorado, Idaho, Nevada, and Virginia). (2) An oxide of lead corresponding to the same formula as litharge (PbO), but having a different physical state.
Properties: It is a yellow powder formed by the oxidation of a bath of metallic lead at approximately 345C so that the oxide formed is not melted. D 9.3, mp 600C. If the oxide is melted, it is converted into litharge.

mass number. The number of neutrons and protons in the nucleus of an atom. Thus, the mass number of normal helium is 4; of carbon, 12; of oxygen, 16; and of uranium, 238. A given atom is characterized by its atomic number, equivalent to the number of protons, which give it its charge and thus determine the kind of element, and by its mass number, which includes the neutrons that make up the remainder of its mass. Helium has 2 protons and 2 neutrons (mass number 4 and atomic number 2). Protons and neutrons each have very close to unit mass, and since the mass change associated with binding the particles together in the nucleus is very small, the mass number is always within 1/10th unit of the atomic weight of the nuclide.
See mass; mass defect; atomic weight.

mass spectrometry. A method of chemical analysis in which the substance to be analyzed is heated and placed in a vacuum. The resulting vapor is exposed to a beam of electrons that causes ionization to occur, either of the molecules or their fragments. The ions thus produced are accelerated by an electric impulse and then passed through a magnetic field, where they describe curved paths whose directions depend on the speed and mass-to-charge ratio of the ions. This has the effect of separating the ions according to their mass (electromagnetic separation). Because of their greater kinetic energy, the heavier ions describe a wider arc than the lighter ones and can be identified on this basis. The ions are collected in appropriate devices as they emerge from the magnetic field.



mass susceptibility. Magnetic susceptibility of a compound per gram.

master batch. A previously prepared mixture composed of a base material and a high percentage of an ingredient (usually a dry powder) that is critical to the product being manufactured. Aliquot parts of this mixture are added to production-size quantities (batches) during the mixing operation. This method permits uniform dispersion of very small amounts (less than 1%) of such additives as dry curing agents in rubber and colorants in plastics and paints. Modifying elements may be incorporated in alloys in this way. Master batches of organic dyes dispersed in rubber or plastic are prepared by manufacturers of colorants for direct use. Master-batched accelerators (mixtures of rubber,

zinc oxide, and accelerator) are commonly used in rubber mixes.

mastic. (1) A solid, resinous exudation of the tree *Pistachia lentiscus,* of recent geologic origin. Found in the Mediterranean area. Soluble in alcohol and ether, balsamic odor, turpentine taste. Used in chewing gum, varnishes, and to some extent in adhesives and dentistry. (2) A soft, putty-like sealant; often packed in cartridges and applied by a gun with a nozzle of appropriate size or in bulk for application by a knife or other spreading device. Such mastics often contain bituminous ingredients or polymerized rosin acids, used for laying floor and wall tiles and similar applications.

mastication. Permanent softening of crude natural rubber and certain other elastomers by application of mechanical energy, as on a roll mill or in a Banbury mixer. The softening is said to be due to formation of free radicals resulting from the rupture of the polymer chain and the addition of oxygen at these active points. The study of this phenomenon has been called mechanochemistry. This "breaking down" of a high polymer substance, first practiced by Hancock in England, is essential in preparing it for the incorporation of curatives and other modifying substances and is an essential operation in the manufacture of useful products from rubber and rubberlike substances.

material. A nonspecific term used with various shades of meaning in the technical literature. It should not be used as a synonym for substance, but is generally used in the collective expressions "raw materials" and "materials handling." The term *material balance.* in chemical engineering denotes the sum of all the substances entering a reaction and all those that leave it in a given time period. *Material* also loosely refers to closely associated mixtures, either of natural origin (petroleum, wood, ores) or man-made (glass, cement, composites).
See substance; engineering material; raw material.

material balance. See material.

materials handling. A general term that includes the methods used for in-plant transportation, distribution, and storage of raw materials and semiprocessed products, as by forklift trucks, elevators, conveyor systems, pipelines, etc., as well as safe practices for storage and movement of toxic and flammable substances.

matte. A product containing a metal sulfide as obtained after roasting and fusion of sulfide minerals. Oxides or metals may also be present. Common examples are copper matte and nickel matte.

matter. Anything that has mass or occupies space.
See mass.
(1) *States*: There are three generally accepted states (phases) in which substances can exist, i.e., solid, liquid, and gas (vapor). From time to time it has been proposed that specialized forms of matter be regarded as states, such as the vitreous (glassy) state, the colloidal state, and the plasma state, but none of these suggestions has gained substantial acceptance.
See phase (1); solid; liquid; gas.
(2) *Levels*: Matter is basically composed of particles in the following levels of size and complexity: (a) subatomic (protons, neutrons, electrons), (b) atomic and molecular (below 10 Å), (c) colloidal (from 10 Å to 1 micron), (d) microscopic, (e) macroscopic, (f) space or celestial. Level (a) is invisible by any means, levels (b) and (c) can be resolved in field-ion or electron microscopes, level (d) lies in the range of the optical microscope, (e) is visible to the naked eye, (f) requires telescopes for detailed observation.
See particle; electron microscope; field-ion microscope.

"Maxaquin" ***[Searle].*** TM for lomefloxacin hydrochloride.
Use: Drug.

"Maxatase" ***[Pfizer]).*** TM for subtilisins.

Mayer's reagent. See mercuric potassium iodide.

"Mazawax" ***[PPG].*** TM for all-purpose emulsifying waxes.
Available forms: Solid and flaked.
Use: In creams, lotions, hair relaxant and hair dipilatory formulas.

MBMC. Abbreviation for monobutyl-*m*-cresol.
See *tert*-butyl-*m*-cresol.

MBT. Abbreviation for mercaptobenzothiazole.

MBTE. Abbreviation for methyl-*tert*-butyl ether.

MBTS. Abbreviation for 2-mercaptobenzothiazyl disulfide.
See 2,2′-dithiobisbenzothiazole.

mCi. Abbreviation for millicurie.
See curie.

MCA. Abbreviation for monochloroacetic acid.
See chloroactic acid.

McFadyen-Stevens reaction. Base-catalyzed thermal decomposition of aroylbenzenesulfonylhydrazines to aldehydes.

McLafferty rearrangement. Electron-impact-induced cleavage of carbonyl compounds having a

Hawley's

Condensed Chemical

Dictionary

THIRTEENTH EDITION

Revised by

Richard J. Lewis, Sr.

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indene, is polymerized at low temperatures with concentrated sulfuric acid. These resins are used principally for floor tile and as ingredients of hot-melt compositions.

Poly(alkyl vinyl ethers) are also produced by low-temperature ionic polymerization. Boron trifluoride in the presence of a trace of water may be used as the catalyst. These polymers and copolymers (Acronal, General Aniline & Film Corp.) are characterized by water solubility and good adhesive properties. They are used as pressure-sensitive adhesives and coatings.

Carbazole, which is obtainable from coal tar, may be reacted with acetylene to yield a polymerizable monomer. Polyvinylcarbazole (Polectron, General Aniline), obtained by bulk polymerization of the monomer, is characterized by excellent electrical properties. It is used to a limited extent as a capacitor dielectric (see Vol. 10, p. 910).

2-Pyrrolidone (see Pyrrole and pyrrole derivatives), obtained by the ammonation of butyrolactone, may be vinylated by acetylene. The *N*-vinyl-2-pyrrolidone obtained may be polymerized in water to yield an aqueous solution of polyvinylpyrrolidone (Kollidon, General Aniline). This polymer is soluble in water and in many polar organic solvents. It is used in hair lacquers, as a substitute for blood plasma, and for the removal of color-forming ingredients in the brewing and pharmaceutical industries.

Compounding of Plastics

Additives such as stabilizers, flame retardants, colorants, plasticizers, reinforcing agents, and processing aids are often added to resins to produce plastics that will provide satisfactory service for the proposed end use. The process of adding these ingredients is called compounding after the term used in natural rubber technology.

Compounding of plastics may be done on a two-roll mill, an extruder, or a Banbury (Farrel Corp.) mixer. Concentrates or master batches may be produced and blended with virgin resin on a mill before final processing. The rolls on a two-roll mill operate at different speeds and temperatures. In spite of the simplicity of the milling operation, extrusion is usually preferred since an extruder can operate continuously to produce strands that may be cut by a rotating knife to produce uniform pellets.

Most organic polymers like natural rubber are liable to be oxidized and degraded by atmospheric oxygen, particularly at elevated temperatures and in sunlight. The energy of ultraviolet radiation from the sun is sufficient to cleave covalent bonds and to bring about oxidation of organic polymers. The susceptibility of polymers to ultraviolet degradation (photolysis) varies from resistant products such as poly(vinyl fluoride) to those that are readily attacked like poly(vinyl chloride) and polypropylene. Commercial ultraviolet absorbers or stabilizers absorb radiation in the ultraviolet portion of the spectrum (300–400 mμ) and convert the radiation to a less energetic wavelength. Many stabilizers also serve as free-radical traps and thus prevent photodegradative propagation which is the reverse of the propagation that occurs in chain-reaction polymerization.

The principal commercial ultraviolet stabilizers are derivatives of 2-hydroxybenzophenone, 2-(2′-hydroxyphenyl)benzotriazole, 2-(hydroxyphenyl)triazine, alkyl (2-cyano-3-phenyl) cinnamates (substituted acrylonitrile), and salicylic acid. The amount of stabilizer used is based on empirical tests and economics and is usually about 0.25% of the amount of polymer present.

Since the rate of oxidative degradation increases as the temperature rises, even in the absence of sunlight, antioxidants are added to the organic polymers to minimize

this type of deterioration during processing and in service. Much of this technology has been developed by rubber technologists and adopted by the plastics industry. Hindered phenols, such as 2,6-di-*tert*-butyl-*p*-cresol, and aryl phosphites are usually added to resins such as polypropylene. Oxidative degradation is also reduced by the addition of carbon black and by processing in the absence of oxygen.

Polymers such as poly(vinyl chloride) are dehydrochlorinated in the presence of sunlight and at elevated temperatures. Lead salts have been used to inhibit this autocatalytic decomposition, but calcium, cadmium, and zinc salts of organic acids such as stearic acid are preferred because of toxicity considerations. Synergistic effects are usually noted when more than one stabilizer is added to a polymer system.

Since one of the major uses of plastics is as a material of construction, consideration must be given to combustibility, flame spreading, and smoke formation. Some polymers such as poly(vinyl chloride) and polytetrafluoroethylene are self-extinguishing at normal burning temperatures but even lightly sized fibrous glass is not completely flame-resistant at elevated temperatures in an oxygen atmosphere. Thus, it is customary to add flame retardants to polymers used in various types of construction.

Flame resistance may be improved if polymerizable chlorine compounds such as chlorendic acid and phosphorus-containing polyols are used as replacements for the acids and glycols normally used in the production of polyesters and polyurethans. Other nonreactive retardants such as antimony trioxide, tricresyl phosphate, and chlorinated polyethylene are often added to the polymer. Combustion, like other types of degradation, is a chain reaction involving free radicals. As in the case of other stabilizers, mixtures of flame retardants may have synergistic effects.

The esthetic properties of plastics are improved by the addition of colorants. Inorganic pigments such as titanium dioxide and organic pigments such as phthalocyanines and dyes may be used. White pigments are often used with other pigments to obtain opaque colors. It is convenient to use a concentrated master batch and to blend this with unpigmented polymer. In many cases uniform dispersion of coloring materials may be obtained if the pigment and finely divided polymer are dry blended before extrusion or injection-molding.

The first recorded commercial use of plasticizers was the addition of camphor to cellulose nitrate to produce celluloid by Hyatt and Parkes in 1868. The principal plasticizers used today are dialkyl phthalates, such as dioctyl phthalate, aryl phosphates, such as tricresyl phosphate, and esters of aliphatic dicarboxylic acids, such as dioctyl adipate (see Plasticizers). Nonvolatile polyesters, butadiene–acrylonitrile elastomers, and epoxidized vegetable oils are also used. The latter also act as stabilizers in poly(vinyl chloride) plastics. Over 1 billion lb of plasticizers are used annually in the U.S. Most of this production is used for plasticizing poly(vinyl chloride).

Plasticizers function by reducing the intermolecular (Van der Waals') forces between polymer chains. The most effective plasticizers have solubility parameters similar to that of the unplasticized polymer. Finely divided polymeric materials obtained by coagulation or spray-drying of polymer emulsions or dispersions are usually coated with a thin layer of surface-active agent which blocks the attack by solvents or plasticizers at room temperature. Dispersions of these polymer particles in liquid plasticizers (plastisols) may be poured into molds. When these plastisols are heated at elevated temperatures (325°F), the plasticizer penetrates into the polymer and a plasticized solid polymer is obtained in the same shape as the mold.

The advantageous use of straw as a reinforcing agent in brick manufacture was

recognized by the ancients. Fillers such as wood flour were used by Baekeland to reinforce phenolic resins. Carbon black is an essential ingredient of the rubber compounders' recipes. Other important fillers are α-cellulose, asbestos, silica, and fibrous glass. The latter is used advantageously for reinforcing both thermoplastics and thermosetting plastics.

That fillers are not simple extenders is demonstrated by the improvement in properties of reinforced plastic composites. For example, fibrous glass has little reinforcing effect unless sizing is removed from the surface of the fibers. The reinforcement is enhanced by the addition of coupling agents such as silanes. Reinforcements may be used as finely divided particles or fibers, roving, and woven textiles. Continuous filaments of graphite and boron and single crystals (whiskers) are used for the production of strong temperature-resistant composites. See Laminated and reinforced plastics; Inorganic refractory fibers.

Because of its combustible nature celluloid cannot be processed at elevated temperatures. Hence, solvents are added to assist forming operations at ordinary pressures. Other processing aids such as mold lubricants are also added to assist plastic processing and fabrication in modern plastics technology.

Processing of Plastics

The principal techniques for converting polymers to useful shapes are compression molding (including transfer molding), injection molding, and extrusion. Specialized processing techniques include casting, blow molding, plastisol molding, powder molding, foaming, calendering, laminating, thermoforming, welding, and numerous conventional fabrication techniques.

Compression Molding. This is a refinement of the classical arts used by the ceramic and hydraulic cement industries. Hydraulic press fundamentals which were developed by Pascal in 1653 were applied to rubber and *cold-molding* compositions in the nineteenth century. The latter usually consist of fillers, such as asbestos, and resinous binders which harden when heated under pressure in a closed chamber (*mold*).

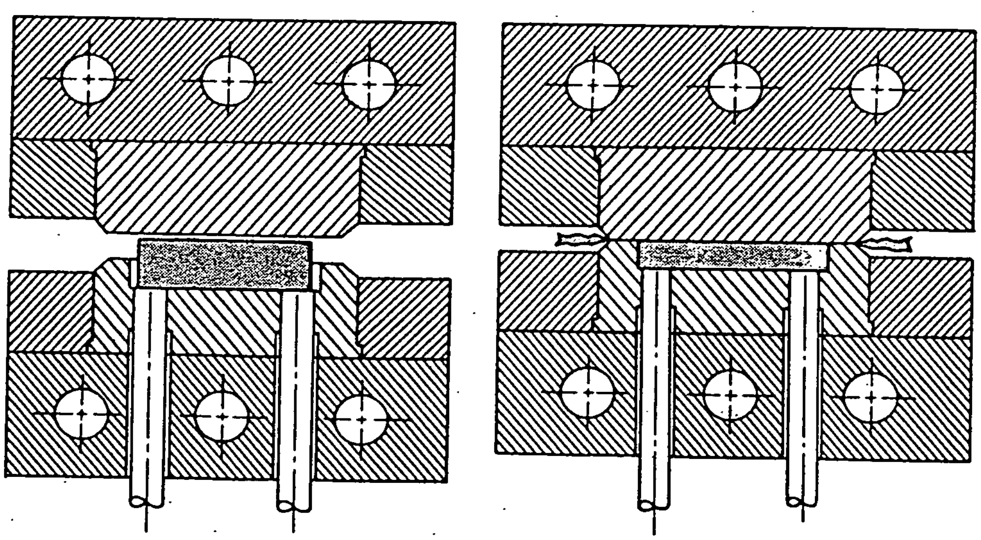

Fig. 1. Compression mold. Open mold with preformed powder shown at left. Molded specimen and flash shown in closed mold at right.

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PLASTICS TESTING

The physical and chemical properties of plastics are governed by the molecular weight, molecular weight distribution, structure, composition, and other molecular parameters of the polymer as well as the nonpolymeric additives such as plasticizers, stabilizers, antioxidants, flame retardants, colorants, fillers, etc, that are added to enhance certain performance characteristics. The properties of plastics are also affected by their previous history because the transformation of resins or compounded plastics into manufactured articles is accomplished through the application of heat and pressure, and involves such processes as calendering, extruding, molding, casting, coating, and laminating. Thus it is not surprising to encounter marked variations in properties of plastics even when dealing with the same class of polymer.

A plastic is defined by the American Society for Testing and Materials as a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in the finished state, and at some stage in its manufacture or in its processing into finished articles, can be shaped by flow.

The reason for testing or characterizing plastics is to measure one or more of their properties and then to relate these measurements to observable or predictable behavior. Thus test methods and characterization procedures are important in quality control, in acceptance testing, and in fundamental and applied studies of polymeric materials. This article is intended to review briefly some of the methods that are frequently used to test and evaluate polymers and plastics. Emphasis has been placed on the accepted methods developed by standards bodies since they play such an important role in the commerce of plastics. No attempts will be made to discuss the tests in detail or to provide complete coverage of the methods that are available because this information may be found in the references cited and in standard texts. See also reference 156.

Thousands of test methods have been developed over the years to examine, identify, analyze, characterize, and measure the properties of plastics and the materials which go into plastics. The choice of the test method usually depends on the specific property to be measured and the intended use of the material. In practice, a variety of tests are often performed on a plastic sample so that data may be obtained on a number of important properties. Frequently, test results obtained on different types of machines will vary even when they are supposed to measure the same property.

Kirk-Othmer

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added, and solvent is removed in an extruder or a drum dryer. The polymer made by coordination polymerization has a molecular weight distribution similar to that of masticated natural rubber and requires no further processing before compounding, whereas that made with butyl lithium is higher in molecular weight and requires even longer mastication than natural rubber.

The properties of the *cis*-1,4-polyisoprenes are, commensurate with their structure, very nearly identical with those of natural rubber, and the synthetic polymers are not only complete replacements for the natural product, but are often preferred because of their greater cleanliness and uniformity. Production has, however, remained relatively small, around 175 million lb. in 1969.

GENERAL REFERENCES

Bean 1967; Kennedy 1968–1969; Anderson 1969; Carpenter 1970; Cunneen 1970.

F. Rubbers Derived from Butadiene

Although also made from alcohol during World War II, butadiene is now derived exclusively from petroleum. Fractionation of the products of cracking petroleum, either for producing olefins or for obtaining high-octane gasoline, yields a cut containing largely hydrocarbons of the butane and butene family. 1-Butene is separated and catalytically dehydrogenated in the vapor phase to butadiene.

Styrene-butadiene rubber (SBR)

Production of SBR (then known as GR-S) was begun in the United States during World War II. The product was designed to be similar to the German Buna-S (Chapter 19) but lower in molecular weight for easier processing. The rubber was made by emulsion polymerization using the so-called Mutual recipe (Table 12-3), at 50°C. After the war, product quality was improved by carrying out the polymerization at 5°C (41°F) with some being made at temperatures as low as −10° or −18°C. These changes were brought about by the use of more active initiators, such as cumene hydroperoxide and *p*-menthane hydroperoxide, and the addition of antifreeze components to the mixture. The product is known as *cold rubber*.

Recently, anionic solution copolymerization of butadiene and styrene with alkyllithium catalysts has been used to produce so-called *solution SBR*.

This product has a narrower molecular-weight distribution, higher molecular weight, and higher *cis*-1,4-polybutadiene content than emulsion SBR. Tread wear and crack resistance are improved, as is economy because oil extension and carbon-black loading can be increased. It seems likely that as the emulsion plants are replaced, new production of SBR will be by the solution process.

Consumption of SBR in the United States remains at about 50% of all rubber use. Total consumption has risen steadily despite significant drops in percentage use in the past decade. Some 2.9 billion lb. was used in 1969 at prices around $0.17–0.18/lb.

Structure of SBR By virtue of its free radical polymerization, SBR is a random copolymer. The butadiene units are found to be about 20% in the 1,2 configuration, 20% in the *cis*-1,4, and 60% in the *trans*-1,4 for polymer made at 50°C, with the percentage of *trans*-1,4 becoming higher for polymer made at lower temperatures. In consequence of its irregular structure, SBR does not crystallize.

Branching reactions due to chain transfer to polymer and to polymerization of both double bonds of a diene unit become extensive if conversion is allowed to become too high or a chain transfer agent is not used in SBR polymerization. However, SBR has been shown to have exactly one double bond per butadiene unit. Thus no extensive side reactions occur during its formation, at least up to about 75% conversion.

Processing of SBR In general, the differences in mastication and vulcanization between SBR and natural rubber are minor. A reinforcing filler is essential to the achievement of good physical properties in SBR. However, some fillers other than carbon black reinforce it moderately well. SBR is compatible with the other major elastomers and can be used in blends. The techniques of oil extension and masterbatching are widely employed. These techniques, as well as the processing of SBR in general, are discussed further in Chapter 19.

Properties of SBR Tire tread stocks made from regular SBR are inferior in tensile strength to those from natural rubber (3000 vs. 4500 psi), whereas those from "cold rubber" are almost equivalent to *Hevea* (3800 psi). At elevated temperatures, however, regular and "cold" SBR lose almost two-thirds of their tensile strength whereas natural rubber loses only 25%. The ozone resistance of SBR is superior to that of natural rubber, but when cracks or cuts start in SBR they grow much more rapidly. Perhaps the most serious defect of both types of SBR for tire uses, however, is its poorer resilience and greater heat buildup. Tread wear of the synthetic material is at

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